



REMOVAL OF PHOSPHORUS FROM HUMAN URINE BY ADSORPTION METHOD USING GGBS

Prakash Kini

Department of Civil Engineering, Manipal Institute of Technology, Manipal, India

Sridevi H

Department of Civil Engineering, Manipal Institute of Technology, Manipal, India

ABSTRACT

A study was undertaken to investigate the response of the adsorbent ground granulated blast furnace slag (GGBS) against phosphorus removal from human urine through batch adsorption experiment. It is necessary to treat human urine at the source, a major contributor of phosphorus in domestic wastewater to reduce adverse effects on aquatic life due to high nutrient manifestation with water bodies. Human urine sample required for the present study were collected from ten young to middle aged persons and 50% diluted with tap water to mimic the flushing system in the source separated toilets. Batch adsorption experiments for various GGBS dosage and contact time were studied with necessary pH corrections. The results show the phosphorus removal efficiency of more than 90% at the dosage of 700g/L and the contact time of 120min. The required pH range to achieve this efficiency was found to be 6-9, a normal pH range of fresh and stored urine as well. The final pH value of diluted human urine was reached around 8.70 from the initial value of 6.28 during the storage period due to urea hydrolysis. This upsurge in pH will evade the necessity of pH correction by artificial means to improve the phosphorus removal efficiency.

Key words: adsorption, GGBS, hydrolysis, phosphorus, urea.

Cite this Article: Prakash Kini and Sridevi H, Removal of Phosphorus from Human Urine By Adsorption Method Using GGBS. *International Journal of Civil Engineering and Technology*, 8(3), 2017, pp. 1061–1069.

<http://www.iaeme.com/IJCET/issues.asp?JType=IJCET&VType=8&IType=3>

1. INTRODUCTION

The phosphorus is an essential nutrient for sustaining all life forms and food production on our planet. Due to the high reactivity nature of phosphorus, it is found as most common molecular form in the environment: phosphate PO_4^{3-} . Phosphorus is the second most abundant mineral nutrient in the body, after calcium. Phosphorus is a limiting nutrient in fresh water aquatic systems. But excessive amount of phosphorus in the water bodies can quickly cause extensive growth of aquatic plants and algal blooms. It is important to notice that the

largest part of nutrients in wastewater stem from urine, with about 80% of the nitrogen and 50% of the phosphorus in wastewater originate from urine [1]. Meanwhile, volume of human urine contributes only 1% to the total volume in domestic wastewater. Among the other constituents in the human urine, phosphorus have a good fertilizer value and it is available in substantial concentrations [1, 18]. Since the regulations towards the effluent discharge and its limits become more stringent day by day, attention to removal of phosphorus has been increased. The major environmental problem such as eutrophication and algae bloom in the water bodies are due to the excessive phosphorus load from industrial, agricultural, household wastes. Due to the high concentrations of nutrients (N, P & K) in the human urine, there is continued interest in removing these nutrients from the urine before it reaches the municipal sewer system. This will reduce the load on wastewater treatment plant.

The ground granulated blast furnace slag (GGBS) is obtained from blast furnace slag, an industrial by-product from Iron and steel industry was used as an adsorbent to remove phosphorus from the human urine in the present study. It is a glassy granular product obtained by quenching molten iron blast furnace slag instantly in water or stream followed by drying and ground into a fine powder.

Most of the studies on phosphorus removal using blast furnace slag were performed on wastewater having relatively very low phosphorus concentrations. Therefore there is a need to investigate the response of slag material in contact with the liquid phase having high phosphorus concentrations especially in human urine, a predominant contributor of phosphorus to the wastewater. The objective of this study includes variances in pH and phosphorus concentrations in human urine during storage period. Also to investigate the effect of adsorbent dosage, pH and contact time on the removal of phosphorus using GGBS.

1.1. The Technology Review

There has been suggested a range of methods to remove phosphorus from the wastewaters. The electro dialysis and reverse osmosis were give efficient results compare to other common phosphorus removal treatment technologies like chemical precipitation (CP), enhanced biological phosphorus removal (EBPR), or a combination of the two [5], but its application has become limited due to the high cost involved. Therefore a CP method remains the leading technology today in the removal of phosphorus [6].

The chemical treatment like struvite-precipitation, a tenacious mineral formed by the ions phosphorus, nitrogen and magnesium removes maximum amount (nearly 100%) of phosphorus from the solution [24]. It is a simple technology using in removal of phosphorus from source-separated urine. The main drawback is that it requires source of magnesium compounds in the precipitation process, which is an additional cost which makes the technology costlier. Also the supernatant shall be treated for a full wastewater treatment scheme including COD removal, nitrification, and denitrification [25].

Biological method of phosphorus removal produces huge volume of sludge and it causes vital operative problems. Also it causes pipe blockages and scaling on the surfaces of treatment units [7, 26]. Furthermore, recent studies [8, 9] have showed that the precipitation of phosphorus during the biological treatment of phosphorus removal could affect Polyphosphate Accumulating Organisms (PAO) in their metabolic action.

Electro dialysis is another method to separate nutrients from source-separated urine [21, 22] and the product obtained can be used as a fertilizer, if the micro pollutants are well within the limits. If not, it requires ozonation to reduce the micro pollutant level. The membranes in the electro dialysis have a pore size less than 1 nm and hence, the treated product will be screened from pathogens. Application of this technology is limited due to the large energy consumption which is not economical.

Adsorption process requires fewer infrastructures and a lesser footprint. It involves separation of substance in one phase and accumulation of that substance at the surface of another phase. The main key factors such as temperature, pH, contact time and the elemental compositions are playing an important role in adsorption process. The selections of adsorbents are based on availability, cost, and reuse & recycling of the material used.

1.2. Phosphorus Adsorption from Human Urine

Bo-Bertil Lind et al. [3] had done a series of experiments using MgO source for struvite crystallization and clinoptilolite and wollastonite adsorbents as ammonia uptake adsorbents, both are natural zeolites. The final product obtained can be used as soil conditioner because of its fertilizer property as it is rich in nutrients. The natural zeolite showed the excellent adsorbent property in the removal of ammonia. The same author was also studied [4] the combined effect of magnesium oxide and zeolite in the removal of phosphorus from human urine. The combined impact from MgO and zeolite at low concentrations gives more efficient results. Precipitation with addition of magnesium at higher pH around 8.5 and at lower pH, the ion exchanger is dominating one in the presence of zeolites. Therefore, the retrieval of phosphorus is a combined effect of magnesium and zeolite addition. Zsofia Ganrot et al. [2] also proved that there is no effect on activated carbon in the adsorption process of phosphorus removal. Even though the above mentioned process includes combination of MgO and zeolite compounds, most of the phosphorus was removed as struvite form by the addition of MgO, this imparts the additional cost to the process, necessitates the research on other economical materials and also the technology.

The primary chemical composition of blast furnace slag includes CaO, SiO₂, alumina (Al₂O₃), MgO and FeO [14]. These constituents are same in all types of blast furnace slag, but relative amount may vary [17]. The occurrence of these components in the adsorbent significantly contributes to phosphorus removal by adsorption and precipitation processes [12, 13]. The amorphous and also the crystalline phases of blast furnace slag can be used efficiently in the removal of phosphate from water solutions [16].

2. MATERIALS & EXPERIMENTAL PROCEDURES

2.1. Adsorbent

The GGBS as an adsorbent in the present study were obtained from locally available market in Shivalli Industrial area Manipal by JSW Cement ltd, India. A scanning Electron Microscopy (SEM) image of GGBS shown in Fig.1 with quantitative EDX (Energy Dispersive X-Ray Spectroscopy) analysis was also summarized in Table1 with most common physical & chemical properties of GGBS. The XRD (X-Ray Diffraction) analysis shown in Fig.2 confirms the amorphous phase of the material.

Table 1 Energy Dispersive X-Ray Spectroscopy analysis for GGBS

Element	O	Si	Mg	Al	Ca
weight %	50.98	12.60	3.37	6.25	26.80
atomic %	68.17	9.61	2.96	4.96	14.31

2.2. Sample Collection and Characterization

Fresh human urine was collected from ten individuals of young to middle aged people without giving considerations specifically such as to their health condition, dietary practices, or consumption of pharmaceuticals. This has been done to simulate conditions of urine volume during collection at random. A part of collected sample was 50 % diluted with tap

water to mimic toilet flushing system and stored for one month. This 50% dilution resembles specifically to the dilution where minimum volume of flush water of about 250mL per flush is employed as like vacuum toilet [18]. The regular gravity flush toilets will consume 7-8 liters of water in each flush and it is of 97% dilution. The same set up was also applied to the remained samples but without dilution. The variances in pH and phosphate concentration in urine samples were observed throughout the storage period. The chemical compositional results are tabulated in Table 2.

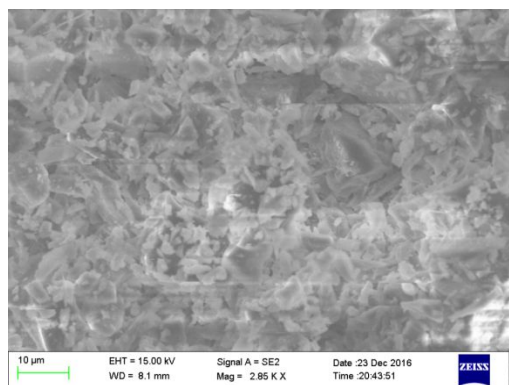


Figure 1 SEM image of GGBS

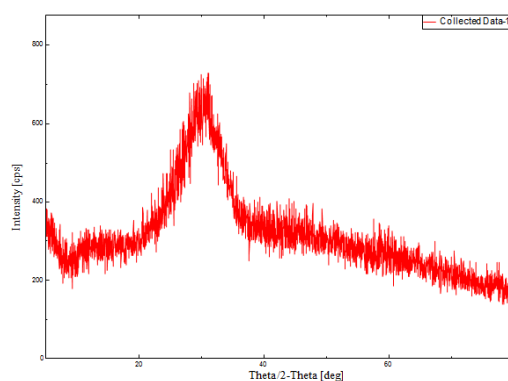


Figure 2 XRD analysis of GGBS

2.3. Batch Adsorption Experiments

Due to the most serious objections [15] to column experiments, the present study uses the single stage batch adsorption system to investigate adsorbent mixing ratio, optimum contact time and pH required to phosphorus removal. Also it involves the performance of adsorbent at various concentration range of phosphorus in human urine. The stored samples were taken throughout the study having initial concentration of phosphate 218 – 226 mg/L. The experiment was performed at constant room temperature by taking 50mL of stored human urine sample. Adsorbent surface contact with solution was made by shaking the mixture using rotary shaker operating at constant speed of 100rpm throughout the study. Phosphate concentration at the beginning of each test and filtered supernatant after adsorption process was analysed by Ascorbic acid method using Merck reagent kit with a Hach-UV spectrophotometer DR5000.

Table 2 Composition of fresh human urine sample and water used for dilution

Measurement	Unit	Fresh human urine	Tap water for dilution
pH	-	6.40	5.30
COD	mgL ⁻¹	8177.00	-
Chloride, Cl ⁻	mgL ⁻¹	4147.00	11.52
Calcium, Ca ²⁺	mgL ⁻¹	80.80	3.20
Magnesium, Mg ²⁺	mgL ⁻¹	96.96	0.96
Ammonical Nitrogen	mgL ⁻¹	460.00	-
Phosphorus, PO ₄ - P	mgL ⁻¹	740.80	<1.00

3. RESULTS AND DISCUSSIONS

3.1. Variances in pH and Phosphate Concentration during Storage

It was observed that the pH crosses 8.40 in both diluted and undiluted samples within 48 hours of storage. Literature describes that the rise in pH due to urea hydrolysis. Urea in the urine sample hydrolyses instinctively, resulting in the formation of ammonia and increase in pH [19]. The decrease in phosphate concentration depends on the calcium and magnesium content in the urine samples [11]. These parameters react with phosphates and precipitates as calcium and magnesium phosphate. The reaction is also influenced by the presence of calcium and magnesium in the tap water used for the dilution. Fig. 3 and Fig. 4 shows the variation in pH and phosphate during the storage period.

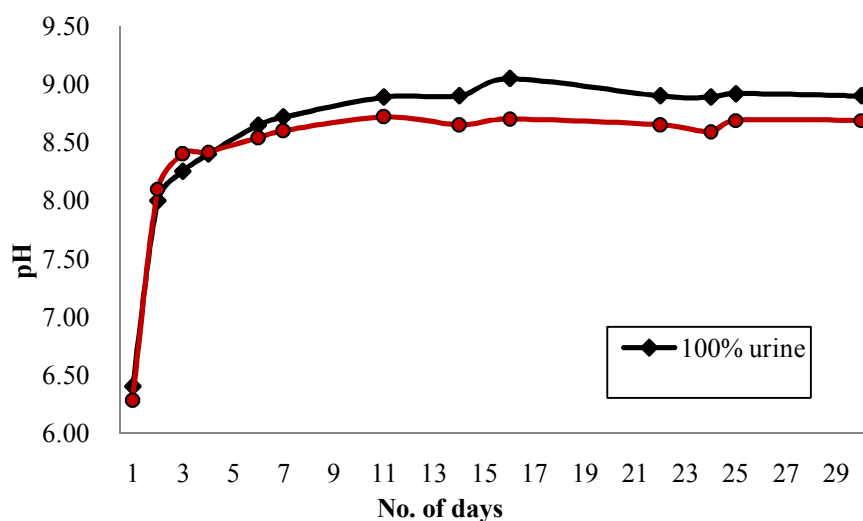


Figure 3 Variance in pH of human urine during storage

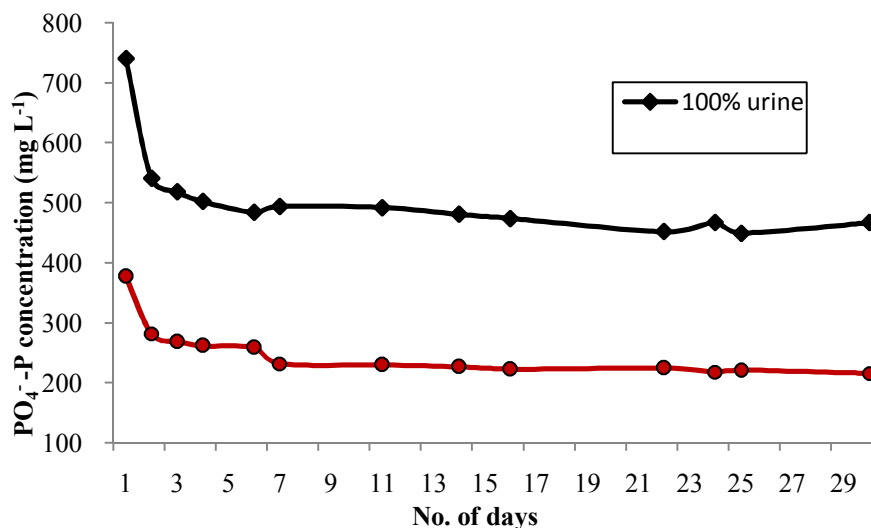


Figure 4 Variance in $\text{PO}_4 - \text{P}$ of human urine during storage

3.2. Effect of Adsorbent Dosage

The different adsorbent dosages starting from 2.5g to 40g were added to the 50ml of urine samples (stored with 50% dilution) taken in conical flask covered with polythene sheets. Initial pH of stored urine sample was found to be 8.65 and phosphate concentration was 226.80 mg/L. The mixture was shaken for 120min and filtered supernatant analyzed for

phosphate concentrations. The percent removal efficiency was increased as the dosage increased. This may be due to more adsorption sites available for adsorption process. It can be seen from Fig 5 that, more than 80% of phosphate can be removed at the dosage of 25g per 50ml of solution and the experiment was continued till the dosage of 40g. It was also observed from the study that more than 95% of phosphorus removal was also possible by increasing the dosage. But considering an economical point of view, a dosage of 35 g per 50ml of solution was fixed to study the effect of essential parameters such as pH, contact time and variant initial concentration of solution in adsorption efficiency as well.

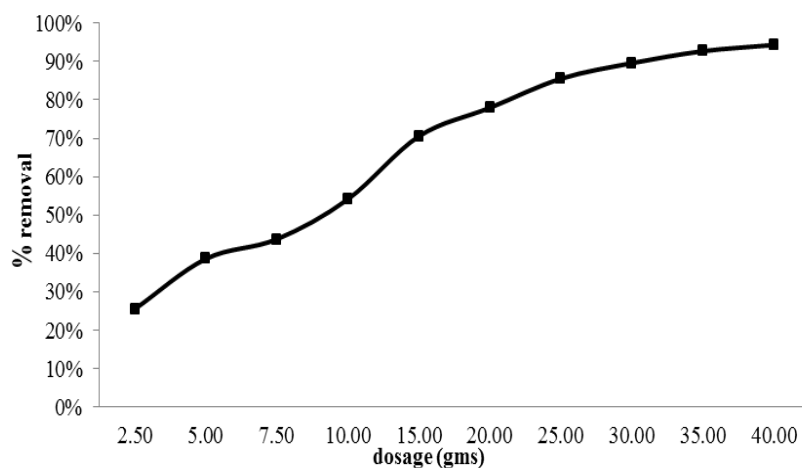


Figure 5 Effect of adsorbent dosage on % phosphorus removal

3.3. Effect of pH

To study the effect of pH in the removal efficiency of phosphorus from the human urine, samples with varying pH values i.e. 6.00, 7.00, 8.00, 9.00, 9.50, 10.00, and 11.00 was taken for batch adsorption experiment for an adsorbent dosage of 35g per 50mL. From Fig.6, it can be seen that there is more than 90% removal efficiency for pH values from 6 to 9. That means the adsorption method can be applied to the urine samples without any pH correction by artificial means as it raise naturally during urea hydrolysis thus makes the technology more economical. However, the effect of initial concentration of phosphorus on adsorption process must be evaluated since it is decreases with time elapsed.

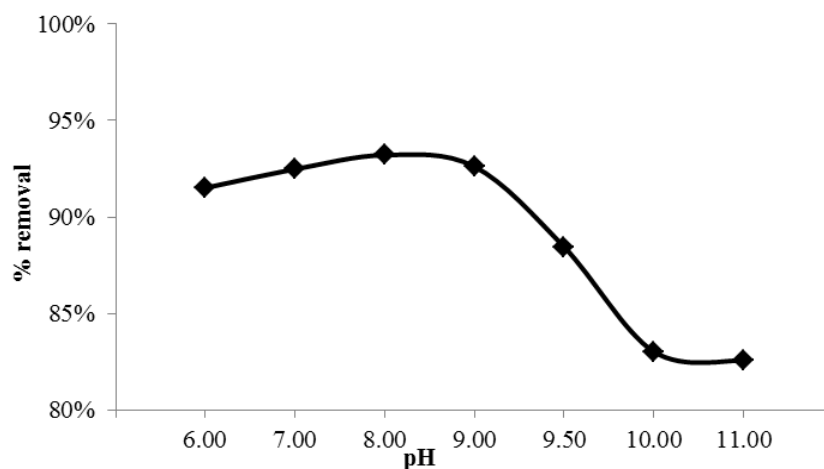


Figure 6 Effect of pH on % phosphorus removal by GGBS

3.4. Effect of Contact Time

The adsorption efficiency of adsorbent on removal of phosphorus from the human urine at various contact time of 30min to 120 min were studied by the batch adsorption experiment. At this stage, adsorbent dosages of 25g and 30g were also taken with 35g per 50 ml of sample. The study shows that the % removal efficiency of GGBS can be increased by increasing contact time and adsorbent dosage as well. It can be seen from Fig.7 that, there is more than 80% of phosphorus has been reduced within the contact time of 90min in all the adsorbent dosage taken.

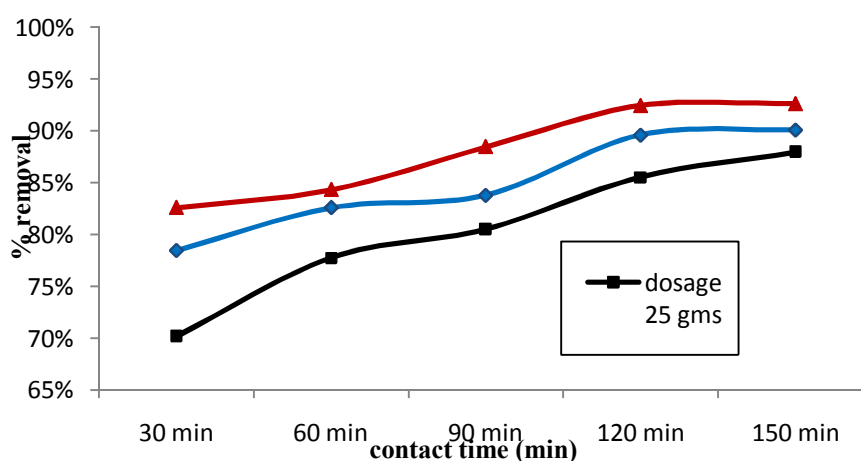


Figure 7 Effect of contact time on % phosphorus removal by GGBS

4. CONCLUSIONS

This study aimed to investigate the adsorption capacity of GGBS on high range phosphorous content from the stored human urine. Batch adsorption experiment results shows that there will be more than 90% of removal efficiency can be attained at a dosage of 700g/L of stored human urine sample at 120min of contact time. This % removal efficiency can be achieved at a natural pH range of human urine. The raise in pH value during storage period due to urea hydrolysis will evade the necessity of pH correction by artificial means to improve the removal efficiency. Meanwhile the effect of initial concentration of phosphorus on adsorption process in response with GGBS must be studied. Because the concentration of phosphorus decreases during the storage period due to the precipitation with calcium and magnesium present in the urine. As it takes high adsorption dosage in the removal of phosphorus, recovery options for the phosphorus loaded GGBS must be investigated to make this technology cost effective.

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